# SYNTHESIS OF IRON OXIDE PIGMENT BY PLANETARY MILLING

A thesis submitted in partial fulfillment
of the requirement for the degree of
**Bachelor of Technology**
in
**Metallurgical and Materials Engineering**
by


## AKASH AGARWAL (111MM0386)
## MANI BHUSHAN (111MM0358)


Under the guidance of

## DR. DEBASIS CHAIRA



**METALLURGICAL AND MATERIALS ENGINEERING**
**NATIONAL INSTITUTE OF TECHNOLOGY**
**ROURKELA (2014-2015)**

# NATIONAL INSTITUTE OF TECHNOLOGY
# ROURKELA

## CERTIFICATE

This is to certify that the thesis entitled ―SYNTHESIS OF IRON OXIDE PIGMENT BY PLANETARY MILLING being submitted by AKASH AGARWAL (111MM0386) and MANI BHUSHAN (111MM0358) for the partial fulfillment of the requirement of Bachelor of Technology degree in Metallurgical and Materials Engineering is a bonafide thesis done by them under my supervision during the academic year 2014-2015, in the Department of Metallurgical and Materials Engineering, National Institute of Technology Rourkela, India.

The results presented in this thesis have not been submitted elsewhere for the award of any other degree or diploma.

(DR. DEBASIS CHAIRA)

METALLURGICAL AND MATERIALS ENGINEERING

DATE: 06/05/2015

NATIONAL INSTITUTE OF TECHNOLOGY

ROURKELA, ODISHA-769008

# ACKNOWLEDGMENT

I would like to express my sincere gratitude to my guide Dr. Debasis Chaira, Metallurgical and Materials Engineering, NIT Rourkela, for giving me the opportunity to work with him and also providing excellent guidance and continuous assistance throughout the project work. His constant criticism, advice, assertions, appreciation were very vital and irrevocable, giving me that boost without which it wouldn't have been possible for me to finish my project. There is not a single day i can remember during my work days which went by without his scrutiny and guidance. I have received endless support and guidance from him, right from the development of ideas, deciding the experiments and methodology of work and this presentation. I am thankful to him for his encouragement throughout the project. I wish to express my deep sense of gratitude to Dr. S. C. Mishra, HOD, Metallurgical and Materials Engineering, NIT Rourkela for giving me an opportunity to work on this project. I would be highly obliged to extend my thanks to Ph.D. scholar Mr. Shashanka R and the M. Tech student for their immense support and help rendered while carrying out my experiments, without which the completion of this project would have been at stake. I would also like to thank all the staff members of MME Dept., NITR and everyone who in some way or the other has provided me valuable guidance, suggestion and help for this project.

DATE: 06/05/2011

AKASH AGARWAL (111MM0386)
MANI BHUSHAN (111MM0358)
METALLURGICAL AND MATERIALS ENGINEERING
NATIONAL INSTITUTE OF TECHNOLOGY
ROURKELA, ODISHA-769008

# ABSTRACT

In the present work, nanostructured $Fe_2O_3$ powders was prepared by mechanical milling in high energy planetary ball mill for different milling time (0 minutes, 15 minutes, 30 minutes and 1 hour) and BPR (6:1 and 10:1). Particle size analysis was carried out to study the size reduction of particles as a function of milling time and BPR and it has been found that particle size decreases with increase in milling time and BPR. X-ray diffraction analysis was carried out to study the change in peak intensity and width of the peak with milling time. Scanning electron microscopy was done to get brief idea about the agglomeration behaviour of the nanostructured $Fe_2O_3$ powder and variation in reactivity of powder with change in BPR. The crystallite size and lattice strain was determined using Williamson-Hall method. The crystallite size of $Fe_2O_3$ powder changes from 445nm to 199nm in case of BPR 6:1 and from 445nm to 146nm in case of BPR 10:1 after 1 hour of milling. The lattice strain continuously increases with milling time in both cases. Zeta potential analysis of prepared iron oxide nanoparticle dispersed in double distilled water was done. It was observed to be higher when milled at BPR 10:1 than that at BPR 6:1 at pH4 of the solution because of uniform dispersion of the finer particles due to increase in surface energy of the particles. The surface plasmon resonance peak in absorption spectra of $Fe_2O_3$ nanoparticle (milled at BPR 10:1 for 1 hour) was observed by an absorption maximum at 430nm. Also the absorption peak was observed to shift to longer wavelength with decrease in crystallite size of the nanoparticle.

**Keywords**: nanoparticle, mechanical milling, ball to powder weight ratio, lattice strain, Zeta potential.

# LIST OF FIGURES

# CONTENT

# 1. INTRODUCTION

Among minerals, iron forms the major part being 6.3% in the earth crust. It exist in combined form, mainly oxygen, in the form of iron oxide. The iron compounds have distinct properties for example its colouration behavior which is due to the transition of electrons between d orbitals [1]. Hematite is the most stable iron oxide and has been used as pigments from long time. These pigments were utilized for beautifiers, craftsmanship painting, dress embellishment, surface adornment, ceramics and so on [1]. Nowadays, hematite is widely used in industrial applications such as colouring paints, plastics, enamels etc. Production of iron oxide pigments has been increasing tremendously due to its increase in demand in construction activity and increasing use of heavy metal pigments. The importance of iron oxide pigment is based on their durability, non-toxicity, chemical stability, low cost and wide variety of colours [2]. Various colours of hematite appear mainly due to variation in crystallinity, particle shape, size and degree of aggregation. There are many literatures available which deals with the different methods employed for the preparation of magnetite, hematite, maghemite and goethetite [2]. These four oxides are mainly used for pigmentation leads to black, red, brown and yellow colours respectively [2].

Because of advancement of different new methodologies in pigmentation and paint industry, finer powder of iron oxide has turned into the significant necessity with particular microstructure attributes. Properties of the material enhance massively when their size is decreased to nano level. Commercially produced hematite nano particles need to be advanced with the goal that we can get superb quality products with least energy utilization and natural impact. Synthesis of iron oxide nano particles through chemical route is regular in industry despite the fact that they are extremely costly and complicated. Moreover, bulk synthesis of pigment is a problem.

Many synthesis routes like hydraulic pressing, high pressure torsion, ultrasonic shot peening, equal channel angular processing are used to refine the structure of metals and alloys by plastic deformation and solid solution mechanism [3]. An alternative method for the production of iron oxide nano particle is the processing of micro sized particle through mechanical milling. Grinding mills include oscillating and vibration mill, attrition jet, planetary mills, all of which are known as high energy mills [4]. Among all, planetary milling is the most simple and widely used plastic deformation method through which one can achieve extreme refinement in the structure of materials in bulk amount. As the name indicates, the container is rotated about two parallel axis similar to the planetary revolution around the sun [4]. The principal behind high energy milling process is very simple: powered materials and grinding media (usually balls) are sealed in a vial and the reduction in size occurs by mechanical activation so close that chemical reactivity and diffusion are enhanced. The rate of particle refinement depends on various milling parameters such as milling time, BPR, PCA, size of balls used, milling speed and many more [3].

# 2. OBJECTIVE

The main objectives of the present study are as:

- Production of the iron oxide ($Fe_2O_3$) nano particles by high energy planetary milling for pigment preparation.
- Study the effect of milling time and ball to powder weight ratio (BPR) on particle size and shape during milling.
- Study the stability of iron oxide particles in distilled water at different pH.
- Study the effect of milling time on absorbance peak wavelength of plasmon resonance.

# 3. LITERATURE REVIEW

## 3.1 Pigments

A pigment is a material that changes the colour of reflected or transmitted light as the consequence of wavelength-particular retention [14]. This physical methodology varies from fluorescence, glow, and different types of luminescence, in which a material transmits light. A pigment should have high tinting strength (mixture of colour with white that increases it lightness) relative to material it colours. Also it must be stable in solid form at high temperature. Non-permanent pigments are called fugitive which disappear over time. Pigments are utilized for shading paint, ink, plastic, fabric, beautifying agents, sustenance and different materials [5]. A differentiation is generally made between a pigment, which is insoluble in its vehicle (bringing about a suspension), and a dye, which either is itself a fluid or is dissolvable in its vehicle [5]. At the point when light is incident on the pigment, parts of the bands are consumed by the chemical bonding of conjugated frameworks and different segments of the pigment. Some different wavelengths or parts of the bands are reflected or dispersed [5]. The new reflected light band makes the presence of a colour. Pigment, dissimilar to fluorescent, can just subtract wavelengths from the source light, never include new ones.

Iron oxide has been used as pigments since long before owing to its advantage of pure hue**,** consistent properties**,** and tinting strength [6]. The building materials industry is the greatest client of iron oxide pigments. Utilizations incorporate concrete cement and mortar on account of their great dispensability and great tinting quality. They are broadly utilized as a part of the assembling of paving blocks, checker tiles, designer tiles, stamped concrete and so on [6]. Paints industry is the second biggest client of iron oxide pigments. Pigments utilized as a part of

plastics need high immaculateness, tinting quality, high heat resistance and great dispensability [6]. Unique applications incorporate that in ceramic colours, cosmetics, cork sheets, rubber, brake linings, drugs, wood polish, fertilizers and cattle feed. New applications incorporate impetuses in petroleum industry, in oil boring apparatuses, in compound shades, duplicate machine powder, and attractive separate materials.

### 3.1.1 Natural and synthetic iron oxide pigment

Natural pigments are products that have been obtained from selected minerals. Iron minerals that are dug for steel must be fit for being mined and lessened to iron on competitive business premise. These minerals are chosen on the premise of iron content and handling financial aspects. It is subsequently abnormal when iron minerals for steel generation are suitable for utilization as mineral pigments. Characteristic colour of resources are chosen for their extraordinary physicochemical characteristics and have the capacity to charge a premium cost over the iron minerals utilized for steel producing [7]. Synthetic pigments, and in this occasion iron oxides, are pigments delivered from fundamental chemicals. A synthetic chemical produces pigmentary particles straightforwardly, rather than the utilization of comminution, the system basic to setting up all common iron oxide pigments [7].

### 3.1.2 Classification

Pigments have been classified on the basis of its colour. Some of the important pigments are as follows [7]:

I) Yellow iron oxide pigments

1) Goethite
2) Lepidocrocite

- Synthetic pigments

1) Goethite (αFeOOH)
2) Lepidocrocite (γFeOOH)
3) Akagenite (βFeOOH)

II) Red iron oxide pigments

- Natural mineral origin

1. Hematite
2. Siderite (calcined)
3. Pyrites (calcined)

- Synthetic pigments

Hematite ($\alpha Fe_2O_3$)

III) Brown iron oxide pigments

- Natural mineral origin

1. Umbers
2. Limonite (calcined)
3. Siderite (calcined)

- Synthetic pigments

1. Blends of hematite, goethite, and magnetite
2. Coprecipitated hematite–magnetite
3. Maghemite ( $Fe_2O_3$)

IV) Black iron oxide pigments

- Natural mineral pigments

1. Magnetite
2. Slate (mixed minerals)

### 3.1.3 Chemical and physical properties required for iron oxide pigment [7]

- Chemical properties :
    1. Nonreactive
    2. Should contain only traces of heavy metals and toxic elements.
    3. Should have high degree of light fastness.
- Physical properties :
    1. Oil absorption: The amount of oil needed to wet out 100 grams of pigment and to make paint with a pigment is called oil absorption [14]. It is expressed in number of grams of oil per 100gm of pigment.
    2. Surface Area: It is defined as the total area taken by the solid surface of the pigment. It is defined as 10 $m^2$ to 30 $m^2$ for 1 gram of pigment. Larger particles having small surface area needs less binder and vice versa.
    3. Particle Size: It can affect the settling characteristics, colour and hide of the pigment. Smaller particles settle slowly and harder to disperse as compared to that of larger particles.
    4. Particle shape: Smaller the particle, greater the surface energy and more likely the chances of reactivity. Shape influences the shade and properties of the pigment.

## 3.2 Mechanical milling

Mechanical alloying (MA) is a strong state powder transforming strategy including repeated welding, breaking, and re-welding of powder particles in a high-energy ball mill [15]. Mechanical alloying (MA) is a powder transforming strategy which permits creation of homogeneous materials beginning from mixed natural powder mixtures [8]. The powders undergo reduction in particle size.

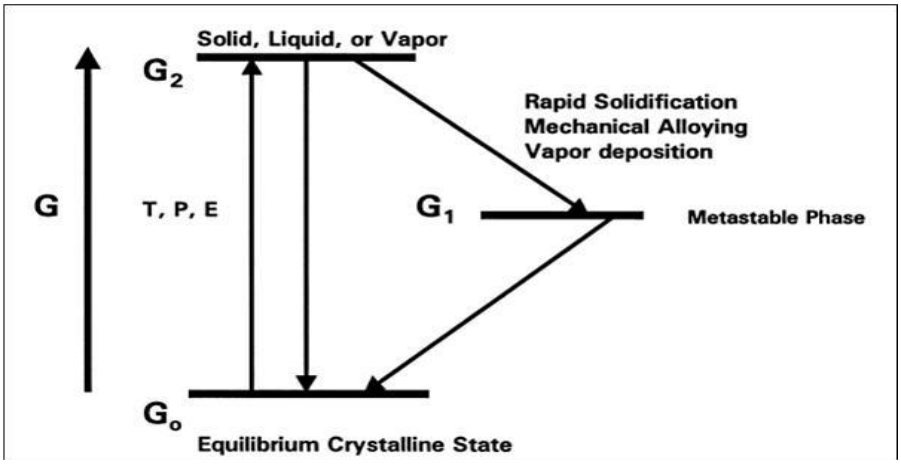



**Fig. 1** The basic concept of "energizing and quenching" to synthesize non-equilibrium particles [8]

### 3.2.1 Stages of mechanical alloying [9]

Mechanical alloying is carried out under different stages as follows:

1. Molecule straightening

This is the first phase of processing and at first the particles get straightened and get to be drop.

2. Welding transcendence

3. Equiaxed molecule development

After this, the lamellar particles stop to be chip like and get to be thicker and adjusted. The shape change is brought about by the work hardening of the powders [9].

4. Random welding orientation

Welding of particles again begins as the sections from the equiaxed particles begin to weld in distinctive introductions and the lamellar structure begins corrupting.

5. Steady state

At last, the structure of the material gets continuously refined as sections are taken from the particles that later weld with different sections in distinctive orientation [9].

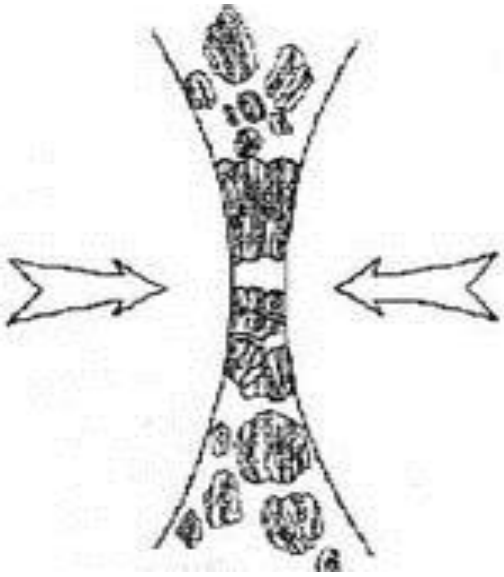


**Fig. 2** Ball-powder-ball collision of powder mixture during milling process [9]

### 3.2.2 Components of mechanical alloying

The genuine methodology of MA begins with blending of the powders in the right extent and stacking the powder blend into the mill alongside the crushing medium (mostly steel balls). This blend is then processed for the desired time span until an unfaltering state has come to when the organization of each powder molecule is the same as the extent of the components in the beginning powder blend [8]. The processed powder is then agglomerated into a mass shape and heat treated to get the coveted microstructure and properties.

The components in mechanical alloying are:

- Raw materials
- Types of mill
- Process variable

### 3.2.2.1 Raw Materials

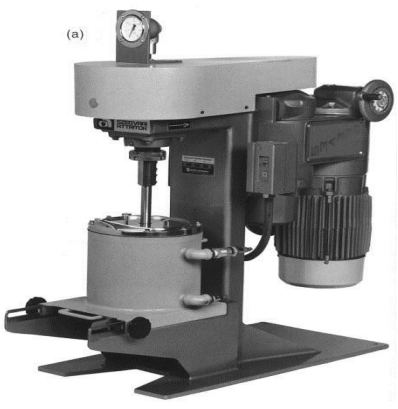
The raw materials utilized for MA are generally accessible economically immaculate powders which have molecule size ranges from 1 to 200 mm [8]. Anyway, the powder molecule size is not extremely basic, with the exception of that it ought to be less than the size of grinding ball. This is on the grounds that the powders molecule size reduces drastically with time and achieves a nano range when processed for couple of minutes [8]. The raw powders come in the general classes of unadulterated metals, expert combinations and prealloyed powder. Infrequently, metal powders are processed via fluid media and this is termed as wet crushing. If there is no fluid included then it is termed as dry crushing. It was accounted that the wet crushing is a better technique as compared to dry crushing for acquiring fine-powder in light of the fact that the solvent is adsorbed at the framed surface of the particles and bring down the surface energy [8].

### 3.2.2.2 Type of mill

There are various kinds of mills depending on their capacity, arrangements for heating, cooling, efficiency of milling. A brief discussion of each type of mill is provided below.

**1.** Attritor mill

A customary ball plant comprises of a pivoting even drum half-loaded with tiny steel balls. As the drum turns the balls fall on the metal powder which is being ground; the rate of meshing increments as the velocity of revolution increases. When the speed is high, then again, the centrifugal force following up on the balls surpasses the power of gravitational force, and balls are stuck to the mass of drum surfaces of the particles and bring down their surface energy [8]. An attritor comprises of a vertical drum with a progression of impellers inside it. Set logically at right angles to one another, the impellers empower the ball charge, bringing on decrease in powder size on account of effect between balls, in the middle of balls and compartment divider, and between balls, instigator shaft, and impellers [8]. A motor pivots the impellers that shake the steel ball in the drum.



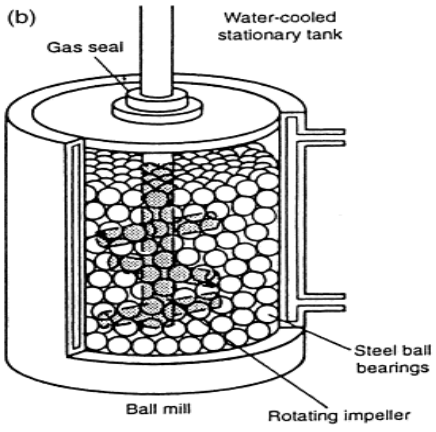




**Fig. 3(a)** Attritor Mill [8]

**Fig. 3(b)** Schematic diagram of attritor mill [8]

## 2. SPEX Shaker Mill

Shaker mills for example, SPEX plants which process around 10 to 20 g of the powder at once, are most generally utilized for lab examinations and for compound screening purposes [8].The regular assortment of the mill has one vial, containing the specimen and grinding balls, secured in the clip and swung overwhelmingly back and forward a few thousand times each moment. The forward and backward shaking movement is joined with sidelong developments of the finishes of the vial. With every swing of the vial the balls sway against the powder and the end of the vial, both processing and blending the specimen. In view of the amplitude (around 5 cm) and rate (around 1200 rpm) of the clip movement, the ball speeds are high (on the request of 5 m/s) and subsequently the power of the ball's effect is abnormally incredible. Subsequently, these mills can be considered as high-energy mill [9].


**Fig. 4** SPEX Shaker Mill [8]

## **3.** Planetary Ball Mill

Planetary ball mill is one in which a couple of hundred grams of the powder can be processed at once. The planetary ball mill owes its name to the planetary motion of its vials. These are organized on a rotating disk and a unique commute component makes them turn around their own particular axis. The centrifugal force created by the vials turning around their own particular axis and that delivered by the pivoting disk  both follow up on the vial assents, comprising of material to be ground and the grinding media [8]. Since the vials and the supporting disk pivot in inverse direction, the centrifugal strengths then again act in like and inverse direction, causing the pounding balls to revolve-over within mass of the vial —the friction impact, trailed by the material being ground and crushing balls lifting off and revolving through the inward balls of the vial and crashing against the restricting inside wall-the impact effect.

**Fig. 5** Planetary Ball Mill [16]

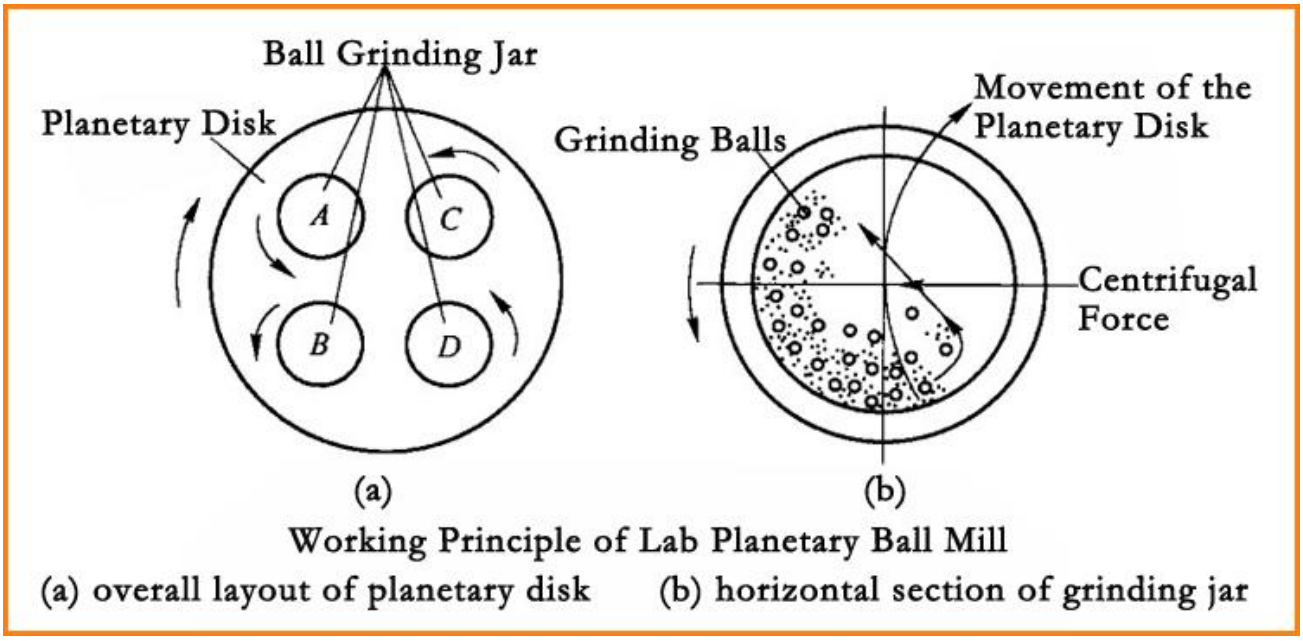



**Fig. 6** Working principal layout of planetary ball mill

### 3.2.3 Process Variables

Mechanical alloying is an intricate procedure and thus includes improvement of various variables to attain the required microstructure. Some of the important parameters are [8]

- Milling container
- Milling speed
- Milling time
- Grinding medium
- Ball to powder weight ratio (BPR)
- Milling temperature

### 3.2.3.1 Milling container

The material utilized for the processing vessel (granulating vessel, vial, container, or disk) is significant because of effect of the crushing medium on the internal walls of the vessel. Some material will be unstuck and get joined into the powder which can adulterate the powder or modify the composition of the powder [8]. In the event that the materials of the pounding vessel differ from that of the powder, then the powder may be polluted with the grinding vessel material. Then again, if the two materials are the same, then the composition may be modified unless safety measures are taken to make up for the extra measure of the joined component.

### 3.2.3.2 Milling speed

It is anything but difficult to understand that more the speed of the mill, higher would be the impact force into the powder. In any case, relying upon the configuration of the mill there are restrictions to the most extreme speed that could be utilized [8]. For instance, in a traditional ball mill, more the speed of revolution, higher the rotational speed of the balls. Over a critical speed, the balls will be stuck to the internal walls of the vial and don't apply impact force. Hence, the greatest pace ought to be just beneath this critical speed so that the balls tumble down to create the highest impact.

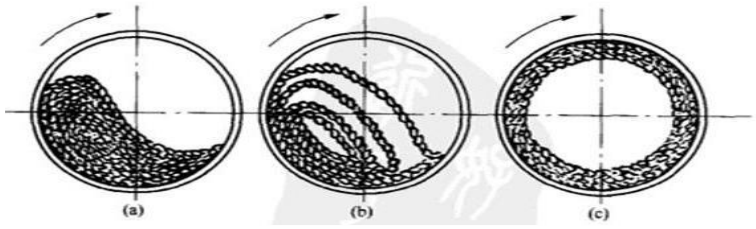



**Fig. 7** Ball starts pinning to the inner wall of the vial as speed of rotation increases, and at critical speed of rotation the balls will be completely pinned to the inner walls of the vial and do not fall down to exert any impact force [10].

### 3.2.3.3 Milling Time

Milling time is the most critical parameter. Typically the time is so picked as to attain to a consistent state between the breaking and cold welding of the nano particles. The processing time depends on the number of factors such as the power of processing, the ball-to-powder proportion, and the temperature of processing [8]. In any case, it ought to be understood that the level of adulteration increases and some undesirable structure obtained if the powder is processed for times longer than needed. Along these lines, it is attractive that the powder is processed only for the obliged length of time.

### 3.2.3.4 Grinding Medium

The size of the steel balls likewise has an influence on the processing efficiency. As a rule, a huge size (and high thickness) of the granulating medium is helpful since the bigger weight of the balls will exchange more effect power to the powder particle [8]. Utilization of steel balls of the same size in a round base vial has been demonstrated to create tracks. Thus, the balls move along characterized direction as opposed to hitting the end surfaces arbitrarily. Consequently it is important to utilize a few balls, for the most part a blend of tiny and bigger balls to ``randomize" the movement of the ball [11].

### 3.2.3.5 Ball-to-Powder weight ratio

BPR is an essential process variable. It can be varied from as low as 1:1 to as high as 220:1.The BPR has a noteworthy impact on the time needed to attain to a specific stage in the powder being processed [8]. The higher the BPR, the shorter is the time needed.

At a high BPR, on account of an increment in the weight extent of the balls, the quantity of impacts every unit time increases and thus more impact force is exchanged to the powder particles.

# 4. EXPERIMENTAL DETAILS

A high energy dual drive planetary mill (DDPM) was used especially to produce nano-structured iron oxide ($Fe_2O_3$) powder. DDPM has a principle shaft of 640 mm (L) long and two steel vials of 50 mm (R) radius which turns about their own particular axis around primary shaft. The planetary mill was connected with two 5HP motors used to drive the primary turning shaft and the vials [16]. The shaft speed and jar speed was taken to be 275 rpm and 620 rpm respectively. All the milling experiments were carried out at 64% of critical speed. Milling of iron ore powder (hematite) was carried out in planetary ball mill in chrome steel container at room temperature. The grinding medium was chrome steel balls of same size (8 mm diameter). Two different BPR (ball-to-powder weight ratio) - 6:1 and 10:1 have been used and the powder was milled for different milling time periods ( 15 minutes, 30 minutes, 45 minutes and 60 minutes ) for each BPR.

For 6:1 BPR:

Weight of iron ore taken = 167gm

Total weight of steel ball = 1000gm

For 10:1 BPR:

Weight of iron ore taken = 100gm

Total weight of steel ball = 1000gm

The steel container and the steel balls were washed with water and properly cleaned so as to remove any particulates if present on the surface of the balls and the container.

Sample Run:

A sample run was done for 15 minutes so that grinding balls and the container gets coated with the iron ore powder to minimize the chances of contamination from outside source.

Preparation of iron ore powder samples:

- After the sample run, the 2 containers were filled with iron ore powder so as to maintain 6:1and 10:1 BPR respectively.
- The containers were then put inside the planetary ball mill and a run for 15 minutes was done.
- After one day, the containers were taken out of the ball mill and a small amount of the iron ore powder samples prepared was collected in plastic pouches.
- The containers were then again put inside the planetary ball mill and the procedure was repeated with run time of 30 minutes, 45 minutes and 60 minutes.

Powdered samples were characterized by X-ray diffraction (XRD) in a Philips PANalytical diffractometer using filtered Cu Kα-radiation ($\lambda = 0.1542$ nm). The X-ray source was operated at a voltage of 40kV and current of 35mA. The diffraction angle was varied in the range of 20-100° and the scanning range was 0.5° per second. Powdered samples that have been prepared were used for further characterizations. Williamson–Hall and Scherrer methods were used to calculate the crystal size and lattice strain of the milled powders sample. JEOL JSM-6480LV scanning electron microscopy (SEM) was used to study the powder morphology and particle size of the iron oxide milled samples.

# 5. RESULTS AND DISCUSSIONS

## 5.1 X-Ray diffraction analysis

Fig. 8(a) shows XRD pattern of $Fe_2O_3$ sample milled for various time in DDPM at BPR 6:1 while Fig. 8(b) shows XRD pattern of $Fe_2O_3$ sample milled for various time in DDPM at BPR 10:1. With the increase in milling time the sharp crystalline peaks starts broadening continuously. This is due to decrease in particle size and increase in lattice strain with the increase in milling time. The ball-powder–jar surface collision results in high stress in the powder particles. Decrease in peak intensity is observed with the increase in milling time which suggests the more refinement of the iron oxide particle and reduction in crystallinity with milling.

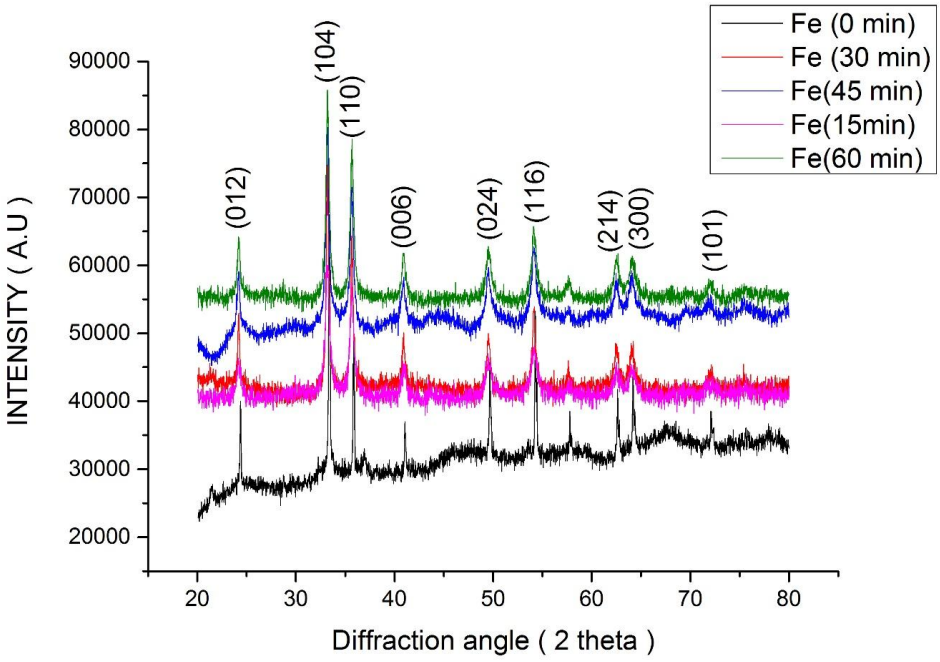



**Fig. 8(a)** XRD patterns of $Fe_2O_3$ powder at different milling hours at BPR 6:1; all the peaks shown are $Fe_2O_3$

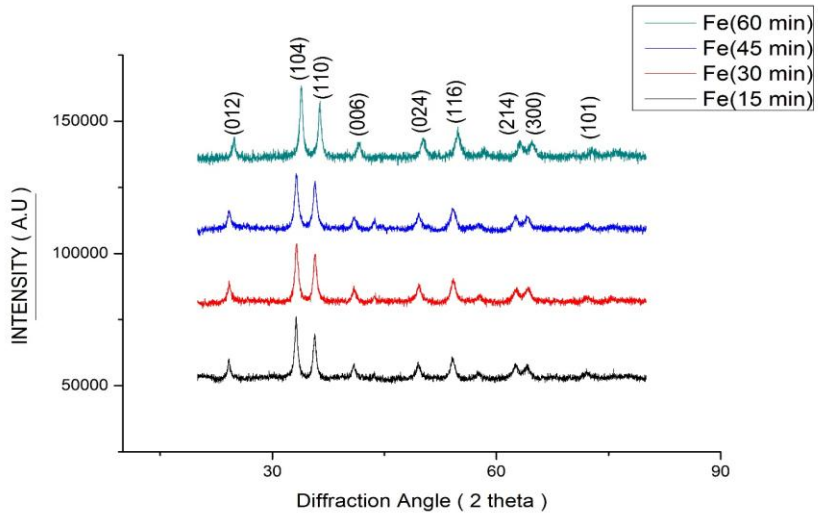



**Fig. 8(b)** XRD pattern of $Fe_2O_3$ powder at different milling hours at BPR 10:1; all the peaks shown are $Fe_2O_3$

On comparing figure 8(a) & 8(b) it can be seen that for same milling time, the peak intensity is decreasing while the peak width is increasing with the increase in BPR. This is due to interaction of greater number of steel balls with the iron ore powder resulting in greater grain refinement and increase in lattice strain with the increase in BPR.

### 5.1.1 Crystallite size and lattice strain calculation

XRD results were used to calculate crystal size and lattice strain of $Fe_2O_3$ powder using Williamson-Hall method. The broadening of the peaks with milling time is observed through XRD patterns which may be due to decrease in particles size, increase in lattice strain and instrumental error [12]. The Williamson-Hall method minimizes the peak broadening errors. The Williamson-Hall equation [12] is given by:

$$\beta \cos \theta = 0.94\lambda/D + 4\eta \sin \theta \qquad (1)$$

where D is crystallite size, β is full width half maxima (FWHM) and η is lattice strain.

For the calculation of lattice strain and the crystallite size, graph was plotted with sin θ in X-axis and β cos θ in Y-axis. The slope and intercept of obtained straight line was than calculated.

Fig. 9(a) and Fig. 9(b) shows the variation of crystallite size and lattice strain of $Fe_2O_3$ powder with milling time at BPR 6:1 and 10:1 respectively. From the figure, it can be seen that lattice strain increases and crystallite size decreases with increase in milling time. This is due to higher interaction of powder-ball, powder-powder and powder-jar surface [12]. Strong collision of powder-ball-jar reduces the crystallite size from 445nm to 199nm in case of BPR 6:1 and from 445nm to 146nm in case of BPR 10:1 after 1 hour of milling. Similarly, the lattice strain increases from 0.016% to 0.51% and from 0.016% to 0.68% in case of BPR 6:1 and 10:1 respectively.

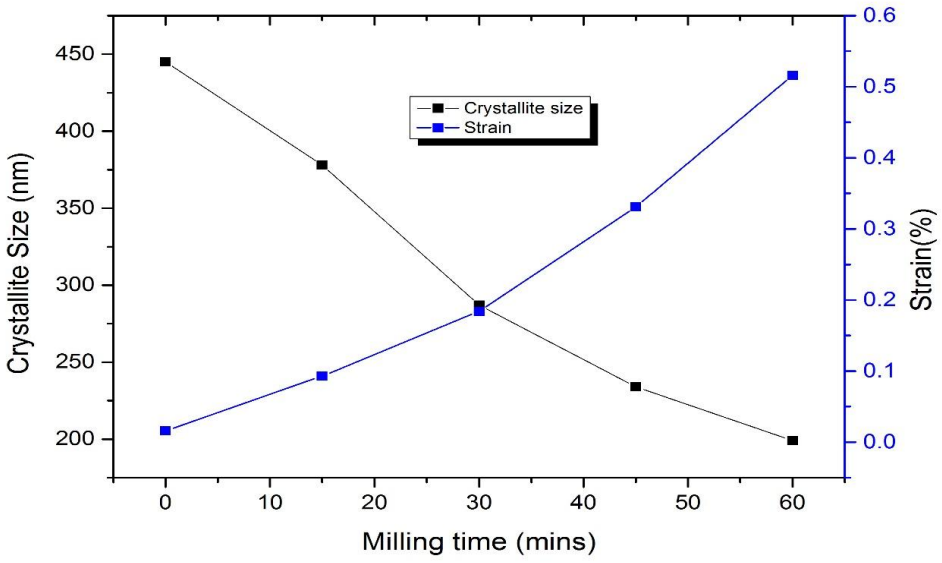



**Fig. 9(a)** Graph showing variation of crystallite size and lattice strain with milling time of $Fe_2O_3$ powder at BPR 6:1

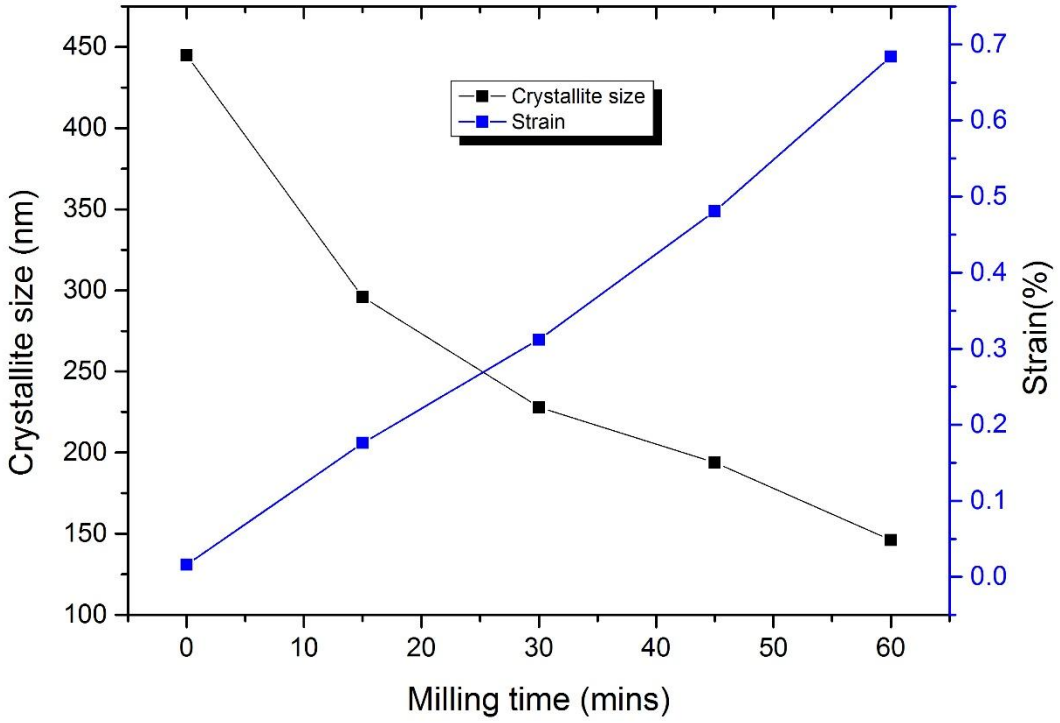



**Fig. 9(b)** Graph showing variation of crystallite size and lattice strain with milling time of $Fe_2O_3$ powder at BPR 10:1

It can be also seen that for same milling time, the $Fe_2O_3$ Powder milled with BPR 10:1 shows lower crystallite size and higher lattice strain as compared with BPR 6:1. This is due to more interaction of steel balls with the iron ore powder in the jar.

## 5.2 Scanning electron microscopy (SEM)

SEM was used to study the microstructure characterization, morphology and particle size of $Fe_2O_3$ milled powder. Both the backscattered electron mode and secondary mode were used. Fig 10 and Fig. 11 shows the SEM micro graphs of $Fe_2O_3$ powder milled for different time period

at BPR 6:1 and 10:1 respectively. It can be seen that the powder particles were bulky and random in size before milling. As milling begins, agglomeration of particles is observed and powder particles get work hardened and refined [16]. Increase in the milling time decreases particle size and very fine powder is observed to be formed.

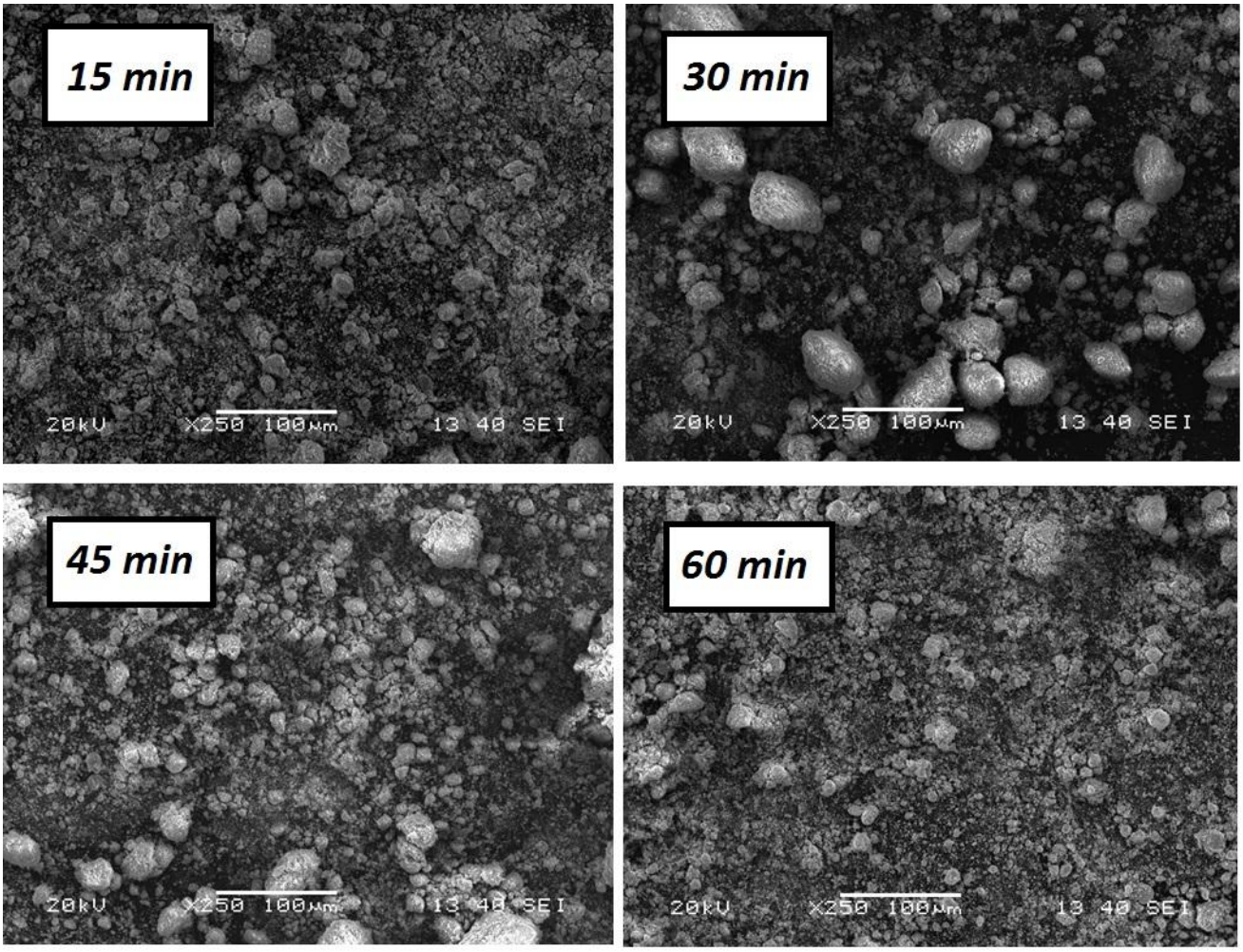



**Fig. 10** SEM micrograph of $Fe_2O_3$ powder milled for different time in DDPM at BPR 6:1

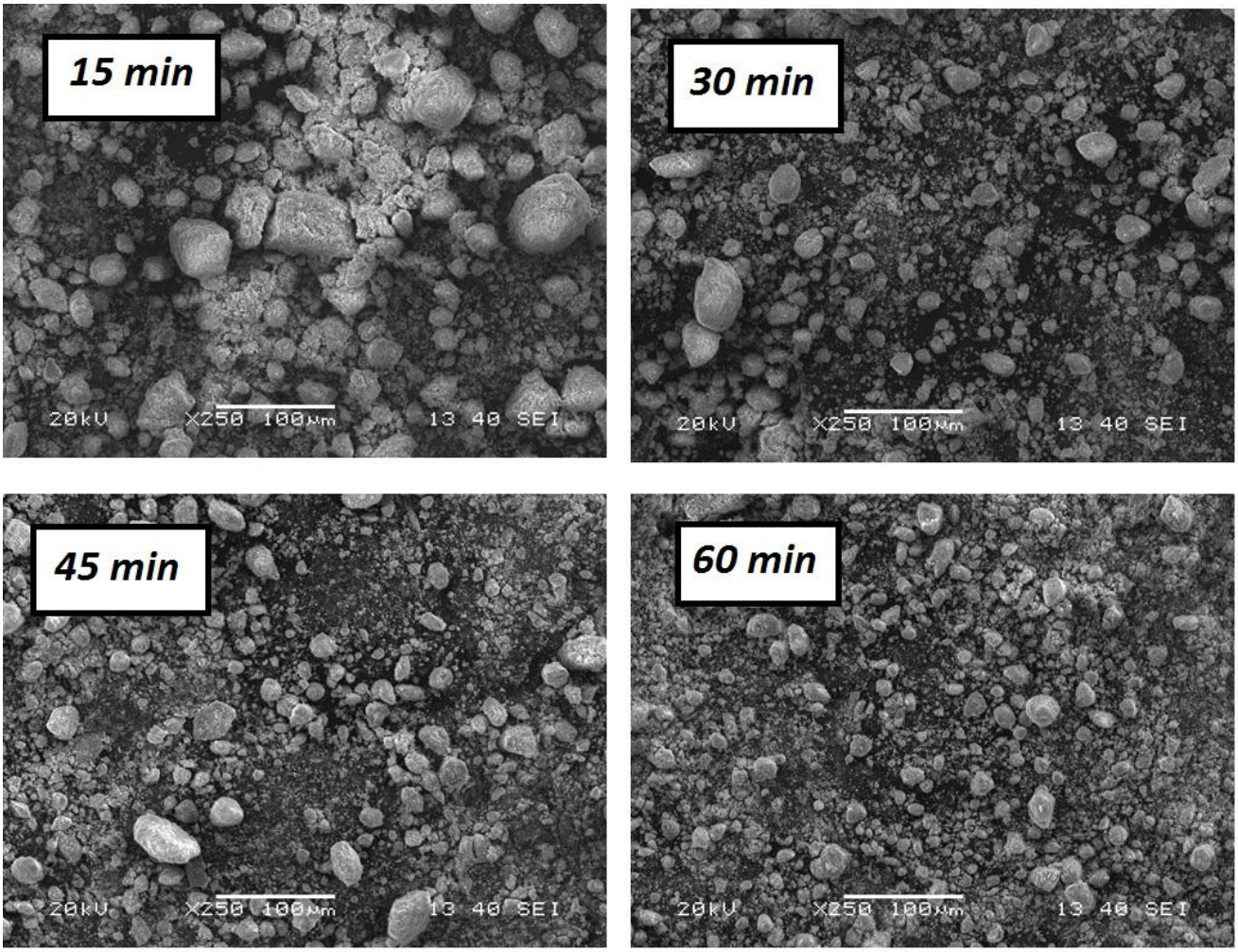



**Fig. 11** SEM micrograph of $Fe_2O_3$ powder milled for different time in DDPM at BPR 10:1

A standard EDX spectrum of iron oxide powder milled for 1 hour at BPR 6:1 and 10:1 was shown in Fig. 12(a) and Fig. 12(b) respectively. The EDX study confirms that the $Fe_2O_3$ powder milled at BPR 10:1 has higher oxygen content as compared to that at BPR 6:1. This is due to small particle size of the powder milled at BPR 10:1 w.r.t that at BPR 6:1. Smaller the particle size, greater is its surface area and surface energy. Hence more is the reactivity of powder with oxygen.

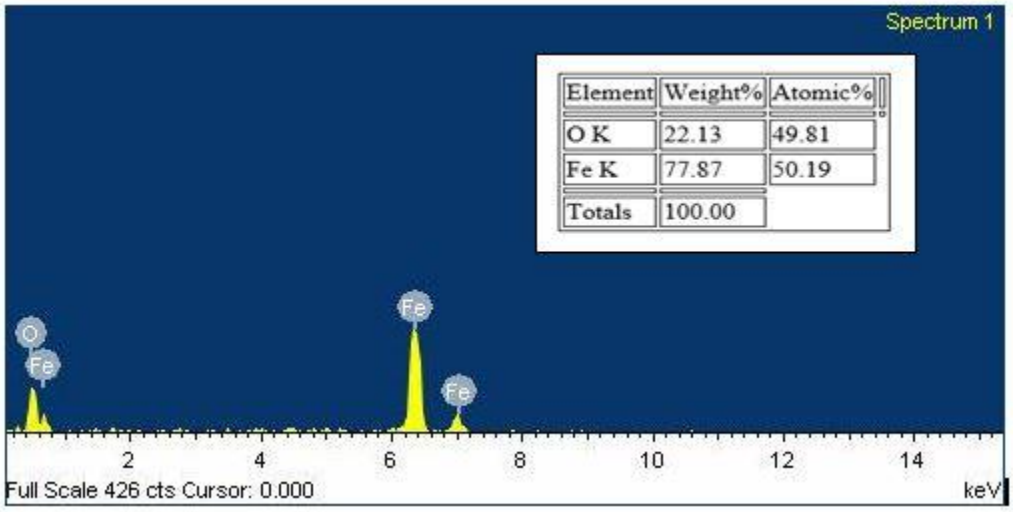



**Fig. 12(a)** EDX Spectra of $Fe_2O_3$ sample milled at BPR 6:1

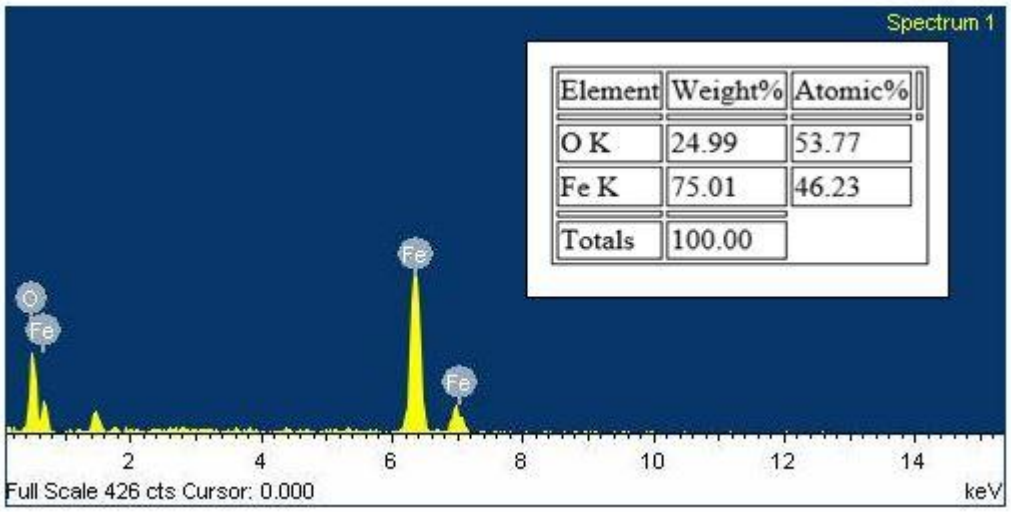



**Fig. 12(b)** EDX Spectra of $Fe_2O_3$ sample milled at BPR 10:1

## 5.3 Particle size analysis

Fig. 13 shows the average particle size plot of $Fe_2O_3$ powder milled for different time period. The graph shows that for same BPR, the average particle size decreases with milling time and for same milling time, the average particle size decreases with the increase in ball to powder weight ratio. This is due to more interaction of steel balls with the iron ore powder in the jar resulting in higher degree of fineness in the powder. The average particle size decreases from 1106nm to 508nm when the $Fe_2O_3$ powder is milled for 1 hour at BPR 6:1 and from 1106nm to 461nm when $Fe_2O_3$ powder is milled for 1 hour at BPR 10:1.

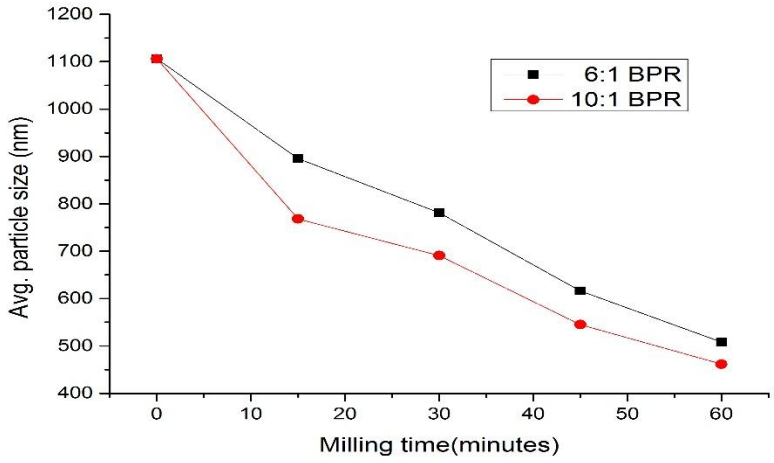



**Fig. 13** Variation of average particle size with milling time and BPR

## 5.4 Zeta potential analysis

Zeta-potential is defined as the electrical potential which gets developed at the solid–liquid interface due to the relative movement between the solvent and the nanoparticle [13]. To study the zeta-potential, the prepared iron oxide nanoparticles were dispersed in double distilled water.

The stability of nanoparticles not only depends on the electrical potential but also the surface charge; hence it is very important to know them. The surface potential of charged particle increases with increase in zeta potential [13]. Fig 14 shows the zeta potential of prepared iron oxide nanoparticle with respect to the pH of the solution in which it is dispersed. From the graph, it can be seen that for same pH of the solution, zeta potential of prepared iron oxide nanoparticle at BPR 10:1 is higher than that at BPR 6:1. This is due to higher number of contact points at BPR 10:1 resulting in higher degree of fineness of the powder. Finer the powder, more is its surface area and surface energy which results in uniform dispersion of the iron oxide nanoparticle in the solution [13].The zeta potential of the prepared iron oxide nanoparticle in the solution with pH4 at BPR 10:1 is 24.8 mV, at BPR 6:1 is 15.9 mV and for unmilled powder is 2.77mV.The unmilled iron oxide powder has lowest zeta potential because it is bulky and tend to settle down easily in the solution.

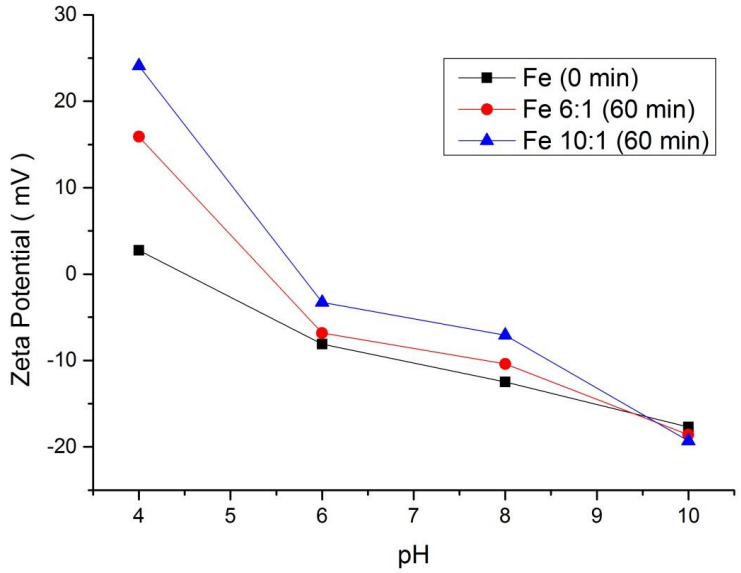



**Fig. 14** Variation of Zeta potential of $Fe_2O_3$ particle with pH of the solution

## 5.5 UV-Vis analysis

UV–Visible spectroscopy ensures the formation of metal nanoparticles in aqueous solution. The colour of iron oxide colloidal solution is reddish brown which is imputed to surface plasmon resonance (SPR) arising due to the collective oscillation of free conduction electrons induced by an interacting electromagnetic field [13]. Fig. 15 shows the UV–Vis spectra of the $Fe_2O_3$ nanoparticle milled for 1 hour at BPR 10:1 obtained. The surface plasmon resonance peak in absorption spectra of $Fe_2O_3$ nanoparticle is shown by an absorption maximum at 430nm. The absorption peak is plausibly related to the electronic transition taking place from valence band to the conduction band [17].

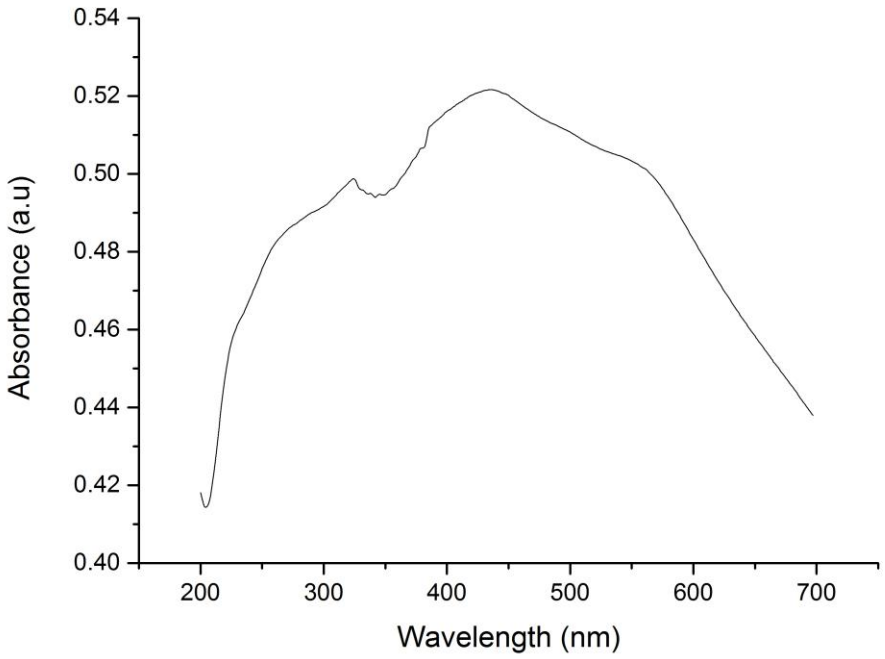



**Fig. 15** UV–Vis spectra of the $Fe_2O_3$ powder milled for 1 hour at BPR 10:1

The absorption peak shift to longer wavelength with decrease in crystallite size [17]. This is observed from Fig. 16(a) and Fig. 16(b) which shows the variation of peak wavelength with crystallite size of $Fe_2O_3$ nano particle milled at BPR 6:1 and 10:1 respectively.

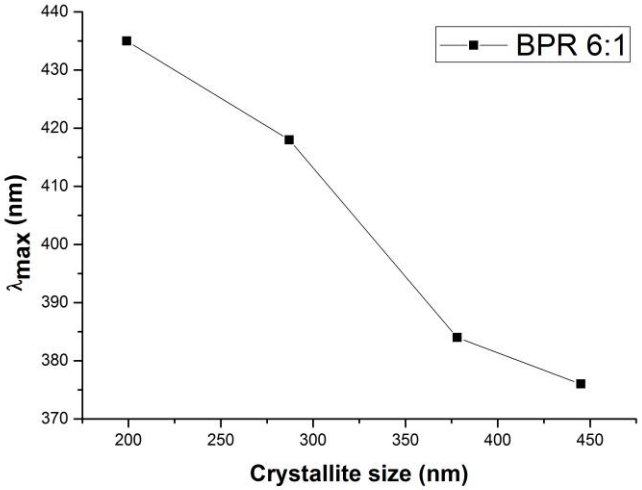



**Fig. 16(a)** Variation of peak wavelength with crystallite size of $Fe_2O_3$ nano particle milled at BPR 6:1

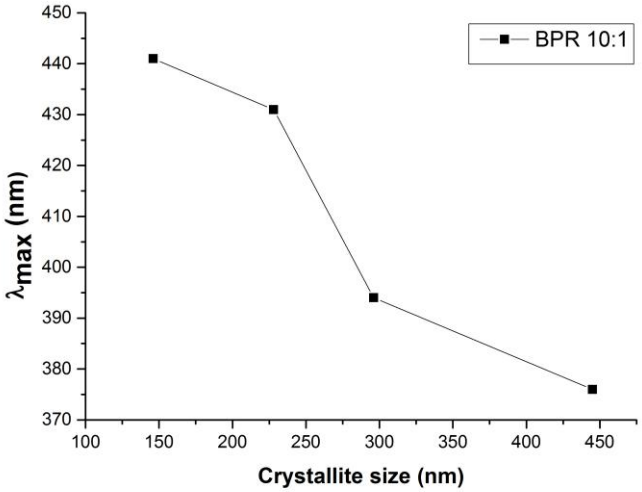



**Fig. 16(b)** Variation of peak wavelength with crystallite size of $Fe_2O_3$ nano particle milled at BPR 10:1

# 6. CONCLUSIONS

Iron oxide nanoparticles were successfully prepared by DDPM after 1 hour of milling. The following conclusions can be drawn from the present work:

- The average particle size of the prepared $Fe_2O_3$ nanoparticle decreases with increase in milling time and ball to powder weight ratio due to higher and frequent collision of steel ball-powder-jar.

- Milling of $Fe_2O_3$ powder carried out at 10:1 BPR shows reduced crystallite size and higher lattice strain as compared to milling carried out at BPR 6:1 due to high impact energy and frequent collision of ball-powder-jar.

- As milling continues, the particle became strain hardened and spherical [16] and then the particle size begin to decrease.

- Milling of $Fe_2O_3$ powder carried out at BPR 10:1 has higher oxygen content as compared to that at BPR 6:1 due to greater reduction in particle size of the powder (increase in the surface area and surface energy) resulting in higher reactivity of powder with oxygen.

- Zeta potential of prepared iron oxide nanoparticle dispersed in double distilled water is higher when milled at BPR 10:1 than that at BPR 6:1 due to higher degree of fineness of the powder. Finer the powder, more is its surface area and surface energy which results in uniform dispersion of the iron oxide nanoparticle in the solution.

- . The surface plasmon resonance peak in absorption spectra of $Fe_2O_3$ nanoparticle is observed by an absorption maximum at 430nm. Also the absorption peak shift to longer wavelength with decrease in crystallite size of the nanoparticle.

# 7. FUTURE SCOPE

- Further tests can be done by changing the other parameters of milling such as milling speed, milling atmosphere, addition of process controll agents, etc and then optimizing the results.

- Grinding kinetics and wet grinding behaviour of $Fe_2O_3$ powder in DDPM can be studied.

- Dispersion behaviour of $Fe_2O_3$ nanoparticle in other solvents other than double distilled water can be studied for its application in paint industry.

- Variation of surface plasmon resonance peak in absorption spectra of $Fe_2O_3$ nanoparticle with respect to concentration of the solution can be studied to gain deeper insight into the colouration behavior of $Fe_2O_3$ nanoparticle.

# 8. REFERENCES

1) Müller M, Villalba JC, Mariani FQ, Dalpasquale M, Lemos MZ, Gonzalez Huila MF, Anaissi FJ, Synthesis and characterization of iron oxide pigments through the method of the forced hydrolysis of inorganic salts, Dyes and Pigments (2015).

2) M.A. Legodi, D. de Waal, The preparation of magnetite, goethite, hematite and maghemite of pigment quality from mill scale iron waste, Dyes and Pigments 74 (2007), p. 161-168.

3) Shashanka. R, D. Chaira, Development of nano-structured duplex and ferritic stainless steels by pulverisette planetary milling followed by pressureless sintering, Materials Characterization 99 (2015), p. 220–229.

4) R.Arbain, M.Othman, S.Palaniandy, Preparation of iron oxide nanoparticles by mechanical milling, Minerals Engineering 24 (2011) 1–9.

5) http://en.wikipedia.org/wiki/Pigment

6) http://www.golchhapigments.com/iron_oxide.html

7) G.Podolsky and A.H. Reid Jr., Pigments, 1453-1458.

8) C. Suryanarayana, Mechanical alloying and milling, Progress in Materials Science 46 (2001), p 4-40.

9) Turker M, Karatas C, Saritas S, Computation of flow behaviors of mechanically alloyed and turbola processed powder PIM feedstock by capillar rheometer.

10) Kilinc Y, Turker M, Saritas S. Investigation of the mechanical properties of iron based super alloys produced by mechanical alloying techniques.

11) Takacs L. In: Suryanarayana C, Processing and properties of nanocrystalline materials. Warrendale, PA: TMS, 1996, p 453-64.

12) R. Shashanka, D.Chaira, Optimization of milling parameters for the synthesis of nano-structured duplex and ferritic stainless steel powders by high energy planetary milling, Powder Technology 278 (2015), p 35–45.

13) S.Rajendrachari, B.E.K Swamy, S.Reddy and D.Chaira, Synthesis of Silver Nanoparticles and their Applications, Anal.Bioanal. Electrochem, Vol. 5, No. 4, 2013, p 455 – 466.

14) http://www.cargohandbook.com/index.php/Pigments

15) S.R.Prima, M.V.Folgueras, M.A.de Lima, D.Hotza, Synthesis and characterization of hematite pigment obtained from a steel waste industry, Journal of Hazardous Materials 192 (2011) 1307– 1313.

16) Shashanka. R, D. Chaira, Phase transformation and microstructure study of nano-structured austenitic and ferritic stainless steel powders prepared by planetary milling, Powder Technology 259 (2014), p 125-136.

17) M.Joshi, A.Bhattacharyya & S.W.Ali, Characterization techniques for nanotechnology apllications in textiles, Indian Journal of Fibre & Textile Research, Vol33, September 2008, p304-317.